

# OPTICAL CHARACTERIZATION ON ITO/TiO<sub>2</sub>/P3HT/ARECA CATECHU/AU FOR THIN FILM HYBRID SOLAR CELL

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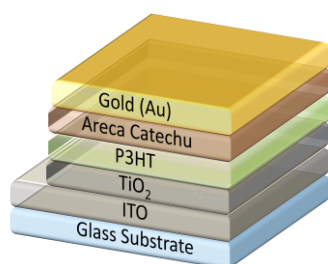
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## Graphical abstract



## Abstract

In this research, dye sensitized solar cell is fabricated by a combination of inorganic titanium dioxide nanoparticles sensitized by a locally available natural dye extract from organic *Areca Catechu* nut. This hybrid solar cells are fabricated accordingly by deposition of ITO/TiO<sub>2</sub>/P3HT/*Areca Catechu*/Au by using electrochemical method. The deposition rates of TiO<sub>2</sub> are varied from 0.05, 0.07, 0.09 to 0.11 vs<sup>-1</sup> whereas the number of scan of each layers are fixed to 5. The absorption spectra analysis is carried out in the wavelength range 200 to 600 nm, showed a wide and significant absorption spectrum in UV and visible regions. Analysis shows that scan rate affects the electrical conductivity of hybrid solar cell. The highest conductivity is recorded at 0.278 Scm<sup>-1</sup> corresponding to the scan rate of 0.07 Vs<sup>-1</sup> at a potential value of 3.5 V.

Keywords: *Areca Catechu*, hybrid solar cells, poly (3-hexylthiophene), titania nanocrystals TiO<sub>2</sub>

## Abstrak

Dalam kajian ini, pewarna sel solar sensitif adalah rekaan oleh gabungan organik titanium dioksida nanopartikel sensitif oleh ekstrak pewarna semulajadi tempatan yang sedia ada dari organik *Areca catechu* kacang. Ini hibrid sel solar adalah direka dengan sewajarnya oleh pemendapan ITO / TiO<sub>2</sub> / P3HT / *Areca catechu* / Au dengan menggunakan kaedah elektrokimia. Kadar pemendapan TiO<sub>2</sub> adalah berbeza-beza dari 0.05, 0.07, 0.09-0.11 vs<sup>-1</sup> manakala bilangan imbasan setiap lapisan adalah tetap hingga 5. Analisis spektrum penyerapan dijalankan dalam julat panjang gelombang 200 hingga 600 nm, menunjukkan spektrum penyerapan yang luas dan penting dalam UV dan kawasan-kawasan yang boleh dilihat. Analisis menunjukkan bahawa kadar imbasan memberi kesan kepada kekonduksian elektrik sel solar hibrid. Kekonduksian tertinggi direkodkan pada 0.278 Scm<sup>-1</sup> yang sepadan dengan kadar imbasan 0.07 Vs<sup>-1</sup> pada nilai potensi 3.5 V.

Kata kunci: *Areca catechu*, hibrid sel solar, poli (3-hexylthiophene), titania nanokristal TiO<sub>2</sub>

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## 1.0 INTRODUCTION

The increasing global demand for energy and the concerns about climate changes have led to a tremendous research works focusing on environment friendly energy sources during the last few years [1]. Due to this concern, the harnessing of solar energy by solar cells, in this context, becomes a very attractive ever-evolving technology due to its indigenous, inexhaustible and sustainability. There are several types of solar cells with different advantages that are being developed by researchers from all over the world such as Plasmonic solar cell [2], Plastic solar cell [3], Polycrystalline solar cell (multi-Si) [4], Polymer solar cell [5], Quantum dot solar cell [6], Solid-state solar cell [7], thin film solar cell (TFSC) [8]. Among all these cells techniques, Dye-sensitized solar cells (DSSCs) emerged as a new generation of photovoltaic devices that have attracted significant attention and have been studied extensively due to their high efficiency, low cost, and facile fabrication [9].

In DSSCs, the dye act as a sensitizer that play a key role in absorbing sunlight. The dye is anchored to the surface of a wide band semiconductor where the charge separation take place due to photo-induced electron transfer from the dye to the conduction band of the semiconductor. Conversion of solar energy to electric energy occurs when the carriers being transported and collected in the conduction band of the semiconductor materials. Sensitizers with broader absorption band allows larger fraction of incident photons from sunlight to be harvested and converted by the system. The highest solar (standard AM 1.5) to current conversion efficiencies is recorded around 10% corresponding to the containing compounds absorbed on nanocrystalline  $\text{TiO}_2$  [10]. Despite its high conversion efficiency, this cells however contains Ruthenium polypyridyl heavy metal complexes, which are non-environmental friendly. Moreover, synthesis of these complexes is complicated and costly and thus limits their large-scale applications in solar cells. Due to this problem, utilization of natural dyes as sensitizers in DSSCs has become a very promising alternative for this technique. Organic sensitizers have shown good conversion efficiencies up to 9.8% which is comparable to the conventional method. Due to their cost efficiency, non-toxicity and complete biodegradation, natural dyes have been a popular subject of intense studies.

## 2.0 METHODOLOGY

### 2.1 Materials and Dyes

All the solvents and the other chemicals employed for the research were reagent and were used as received without any further purification. The conductive glass plate (ITO, Indium doped  $\text{SnO}_2$ ,

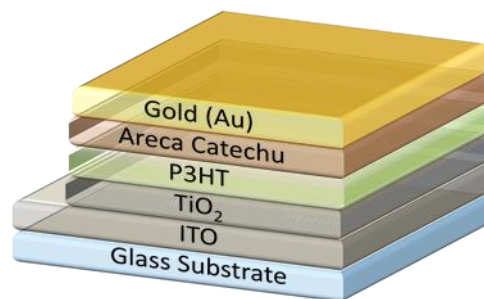
sheet resistance  $7 \Omega/\text{sq}$ ) and titanium oxide nanocrystals,  $\text{TiO}_2$  NCs were purchased from Magna Value Sdn. Bhd. and Sigma Aldrich Sdn. Bhd.; respectively. Meanwhile, poly(3-hexylthiophene) (P3HT) was synthesized accordingly as reported [11]. The ITO glass substrates were cut into  $2 \text{ cm} \times 2 \text{ cm}$  for this research purposes.

### 2.2 Preparation of Titanium Dioxide Nanocrystals, $\text{TiO}_2$ NCs Solution

The  $\text{TiO}_2$  solutions were made using 100 ml 0.5 M  $\text{TiO}_2$  nanoparticles anatase structures and were prepared by dissolved 3.994 g of  $\text{TiO}_2$  in deionized water under magnetic stirring. Then, the solutions were treated with 0.035 M acetic acid for better surface morphology of  $\text{TiO}_2$ . A macroscopic phase separation or aggregation of the inorganic nanoparticles and a bad interfacial contact between inorganic and organic materials will occurred if both materials are incompatible, which leads in low efficiency of the charge transfer from organic to inorganic materials and easy interfacial charge recombination as reported [12]. Thus, modification of  $\text{TiO}_2$  with acetic acid was expected to improve the surface morphology and reduce the aggregation of  $\text{TiO}_2$  nanoparticles.

### 2.3 Preparation of Areca Catechu Dyes Solution

*Areca catechu* nut from tropical palm contains gallic acid, tannin, catechin, alkaloids, fat and gum [1]. Samples of areca catechu nuts are first cleaned with distilled water and cut into smaller pieces. The samples are then placed in a vacuum dryer at temperature around  $60^\circ\text{C}$  for couples of days. The dried samples are crushed into fine powder by using a laboratory mortar. The extract solution is prepared by the addition of approximately 250g of powdered sample into 50 mL of ethanol (95% purity). The mixture was kept at room temperature with the absent of sunlight for a week to make sure the mixture is homogeneously dissolve. Next, the mixture was filtered to remove the solid residue from the dye solution. Finally, a dark brown extract of *Areca Catechu* is collected and used as a dye sensitizers.



**Figure 1** Schematic diagram of organic photovoltaic cell design

## 2.4 Fabrication of Hybrid Solar Cells

The photoanodes is fabricated by depositing Titanium Dioxide (TiO<sub>2</sub>) thin film layer on ITO coated glass substrate by electrochemistry method using the Electrochemical Impedance Spectroscopy (EIS) PGSTAT302. A typical electrochemical impedance experimental set-up consists of an electrochemical cell (the system under investigation), a potentiostat/galvanostat and a General Purpose Electrochemical System (GPES). Prior to the deposition process, the slide is subjected to a sonication treatment at 450 °C for 120 minutes to improve the electronic contact between the TiO<sub>2</sub> nanoparticles. The photoanodes is rinsed with distilled water and ethanol, and then allowed to dry in a clean sealed container. Then, a layer of poly 3-hexylthiophene (P3HT) is deposited on the sample as a polymeric hole transporter in this system. The photoanodes is then soaked in *areca catechu* nut dye for 3 hours to adsorb dye onto the surface. A thin layer of gold (Au) is used as counter electrode and deposited on the entire conductive side of the areca catechu layer. Finally, the whole DSSC layer is kept for 24 hours in the dark sealed container with the absent of light.

The preparation of these particular thin films layer by electro-polymerization using cyclic voltammetry method is studied. By using the GPES software interface, cyclic voltammetry (Staircase) is set to be run at 0.05 V, 0.05 Vs<sup>-1</sup>. The cyclic of the process is fixed at 5 number of cyclic or also known as scan. The number of cyclic determined the different deposition thickness of the layers. Figure 1 shows the schematic diagram of DSSC layers accordingly.

## 2.5 Characterization and Measurement

The absorption spectra of the photo-electrodes were recorded by UV/VIS spectrophotometer (Perkin Elmer, Lambda 25) in the range of 200 nm to 900 nm. Meanwhile, the chemical structure of *Areca Catechu* dye solution was examined by FTIR technique (Model NICOLET 380 FT-IR). Photoelectrical performance of the DSSC was examined by using two point probes (MU SCS-4200-Keithley). This technique is used to measure the current, when voltage is applied from reverse to forward bias across the system. The measurement of I-V curve was recorded using solar illumination direct from the sun with the intensity reading of 100 Wm<sup>-2</sup>. Total energy conversion efficiency of the hybrid solar cell,  $\eta$  is calculated using equations 1 and 2. Input power,  $P_{in}$  is defined as multiplication of incident ray intensity (100 Wm<sup>-2</sup>) with effective surface area (4.0 x 10<sup>4</sup> m<sup>2</sup>) of the hybrid solar cell.

$$P_{max} = I_{max} \times V_{max} \quad (1)$$

$$\eta = \left[ \frac{P_{max}}{P_{in}} \right] \times 100\% \quad (2)$$

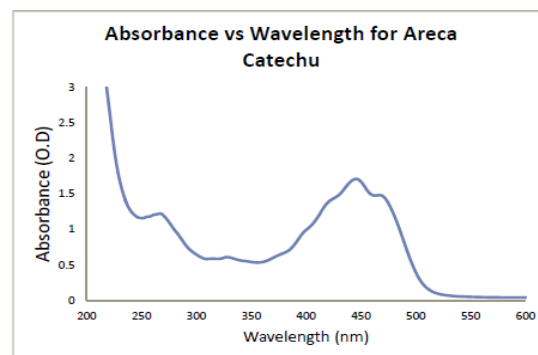
While, the energy band gaps of the thin films were calculated by using Equation 3, where,  $h$  is Planck's constant,  $c$  is the velocity of light and  $\lambda$  is the emitted wavelength in photoluminescence spectrum.

$$E_g = \frac{hc}{\lambda} \quad (3)$$

## 3.0 RESULTS AND DISCUSSION

### 3.1 UV-VIS Spectroscopy Analysis

Pure extract of *Areca Catechu* is deposited on the sample surface in order to enhance the absorption of photon energy by the proposed DSSC system. In this study, the UV-VIS absorption spectrum of *Areca Catechu* solution is recorded in the wavelength range from 200 to 600 nm to indicate the absorption of ultraviolet-visible spectrum. Figure 2 show the UV-Vis absorption spectra of pure and natural dye solution extracted from *Areca Catechu* samples. It is shown that *Areca Catechu* has a broad and strong absorption in the UV region (253-310 nm) and blue region (438-465 nm) with the maximum peak recorded at 450 nm. This spectra indicates the absorption of light in both UV and visible region by the natural dye extract and lead to enhancement of energy absorption efficiency of DSSC system.



**Figure 2** UV-Vis absorption spectra of pure and natural dye solution extracted from *Areca Catechu* samples

### 3.2 FTIR Analysis

The Fourier Transform Infra-Red (FTIR) spectra of natural dye *Areca Catechu* extract is shown in Figure 3. Based on the spectra, the absorption peak at 679.5 cm<sup>-1</sup> is assigned to the cis-disubstituted alkene and the peak recorded at a wavenumber of 736.5 cm<sup>-1</sup> correspond to C-H bond ortho-aromatic ring. The absorption peaks at 1072.8 cm<sup>-1</sup>, 1655.9 cm<sup>-1</sup> and 2364.1 cm<sup>-1</sup> in the natural dye extract correspond to the functional groups of C-O alkoxy, C=O stretching carbonyl and triple bond (C≡C) alkynes respectively. The absorption peaks recorded at the wavenumber between 3438.2 cm<sup>-1</sup> to 3904.2 cm<sup>-1</sup> are assigned to

O-H stretching vibration mode of water molecule contained in the solution.

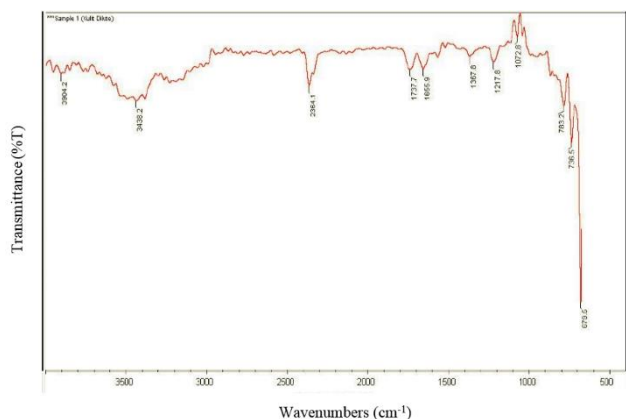


Figure 3 FTIR spectra of Areca Catechu natural dye solution

### 3.3 Redox Behavior and Stability

The cyclic voltammograms (CV) for different deposition rates are obtained during electrodeposition of TiO<sub>2</sub> film on ITO coated glass substrates as presented in Figure 4. Scan rate effect on the electropolymerization, morphology and electrochemical impedance spectroscopic behavior of substrate is examined. In this study, electro-growth process is achieved by applying various scan rates starting from 0.05 Vs<sup>-1</sup>, 0.07 Vs<sup>-1</sup>, 0.09 Vs<sup>-1</sup> to 0.11 Vs<sup>-1</sup> respectively. Based on result, cyclic voltammogram of the sample reveals a redox reaction with broad and symmetrical redox waves. Electro-growth of TiO<sub>2</sub> obtained with different scan rates showed similar redox behavior. As the scan rate of TiO<sub>2</sub> increases, the  $k_{ec}$  is also increase.

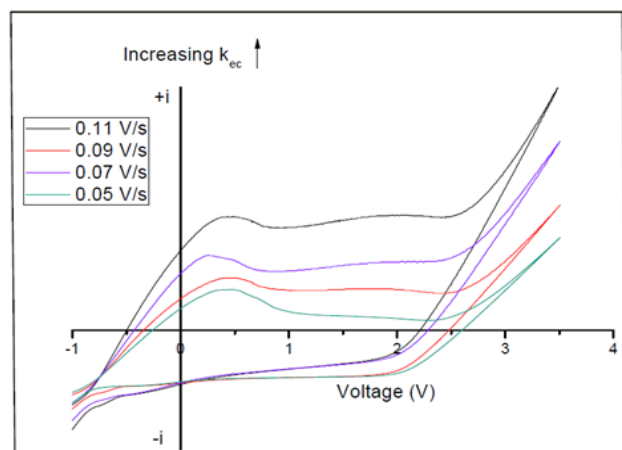


Figure 4 Cyclic voltammogram electro-deposition of TiO<sub>2</sub> film on ITO coated glass substrates run at 0.05 Vs<sup>-1</sup>, 0.07 Vs<sup>-1</sup>, 0.09 Vs<sup>-1</sup> to 0.11 Vs<sup>-1</sup>

## 5.0 CONCLUSION

A natural dye extract from locally available *Areca Catechu* nut is successfully used as an organic dye sensitizer for TiO<sub>2</sub> nanoparticles in DSSC system. UV-Vis absorption spectra of *Areca Catechu* solution shows a wide and significant absorption spectrum in UV visible region. EDX analysis shows that Ti and Oxygen contribute 89.63 % of the total atomic percentage, indicating the purity of TiO<sub>2</sub> nanoparticles deposited on the surface of ITO substrate. Analysis shows that scan rate affects the electrical conductivity of hybrid solar cell. The highest conductivity is recorded at 0.278 Scm<sup>-1</sup> corresponding to the scan rate of 0.07 Vs<sup>-1</sup> at a potential value of 3.5 V. In this study, the highest efficiency of ITO/TiO<sub>2</sub>/P3HT/*Areca Catechu*/Au hybrid solar cell is recorded at 0.021 %. Total energy conversion efficiency of organic DSSC is relatively low compared to non-organic DSSC due with its low open circuit voltage. This phenomenon occurs due to the possible pathways recombination of electron/dye cation and the adsorption of acidic dye environment. The total energy conversion efficiency of organic DSSC can be improved by replacing different additives that might result in greater open circuit voltage.

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